



## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Compositions comprising Crystalline Linear Polyesters

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to compositions comprising one or more crystalline linear polyesters obtained by the polymerization of  $\beta$ -lactones.

Processes are known for the polymerization of lactones to crystalline linear polyesters with a high molecular weight (refer to, for example U.S. patent specification 3,021,309, British patent specifications 766,347 and 1,028,928, French patent specification 1,231,163. These polyesters are valuable thermoplastic polymers from which with the aid of known shaping techniques useful shaped objects can be made, such as foils, sheets, plates, profiles, tubes, fibres, threads and solid or hollow pieces. In technical practice such products from crystalline thermoplastic polymers are usually manufactured under conditions where crystallization of the polymers takes place. However, this crystallization of the said polyesters may readily lead to the formation of inhomogeneous crystalline structures in which spherulites with undesirably large dimensions occur. Too large spherulites in general prevent the formation of polyesters with attractive physical and mechanical properties.

In this connection it is of importance to have means available which enable the crystallization performance of the polyesters to be influenced in such a way that during crystallization the spherulite size can be considerably reduced.

The desired effect on the crystallization performance can be obtained by crystallizing the

polyesters not as such, but in the form of compositions containing in addition to the polyesters also substances which have a nucleating action.

According to the invention certain compounds have been found to possess the desired nucleating action, which compounds may be classified into the categories (a) and (b) further defined hereinafter.

The invention therefore relates to compositions comprising one or more linear crystalline polyesters obtained by polymerization of  $\beta$ -lactones and at the same time one or more compounds of one of the said categories. These compositions are novel. Furthermore, the invention relates to a process for the preparation of the novel compositions and to a process for the preparation of compositions which as compared with the said polyesters as such have improved physical and mechanical properties, as well as to compositions obtained by this process and objects which consist entirely or partly of the latter compositions.

The compositions according to the invention are compositions comprising one or more crystalline linear polyesters obtained by the polymerization of  $\beta$ -lactones and one or more compounds of the following categories:—

(a) alkali metal chlorides, bromides or iodides or boron nitride, and

(b) salts of mono-, bi- and trivalent metals and aromatic carboxylic, sulphonic or phosphinic acids.

The term "crystalline linear polyesters" is used in this specification to denote those linear polyesters which, as shown by X-ray analysis, have a degree of crystallinity of at least 30%. However, special preference is given to polyesters with a degree of crystallinity of at least 60%.

Particularly eligible polyesters are the polymers obtained by polymerization of  $\alpha,\omega$ -dialkyl- $\beta$ -propiolactones in which each of the alkyl groups contains at most 4 carbon atoms, in-

- cluding those cases where the two alkyl groups and the  $\alpha$ -carbon atom of the lactone ring are combined to form one cyclic structure, such as for instance 2-oxa-4-spiro[3,6]-decanone-1.
- 5 The most important representative of the  $\alpha,\alpha$ -dialkyl- $\beta$ -propiolactones is  $\alpha,\alpha$ -dimethyl- $\beta$ -propiolactone.
- The term "polymerization" used in this specification should be taken to include both
- 10 homo- and copolymerization. Copolymerization reactions may be reactions of different lactones inter se, for example copolymerization of  $\alpha,\alpha$ -dimethyl- $\beta$ -propiolactone with  $\beta$ -propiolactone, or reactions of  $\beta$ -lactones with
- 15 one or more suitable other comonomers, such as lactams, for instance caprolactam, and epoxy compounds, for example ethylene oxide, propylene oxide, epichlorohydrin, glycidyl ethers and glycidyl esters.
- 20 The compounds belonging to category (a) mentioned hereinbefore are boron nitride and the chlorides, bromides and iodides of alkali metals, among which the sodium and potassium chlorides are particularly recommended.
- 25 The compound in this category (a) having the strongest nucleating action is boron nitride.
- In compounds of category (b) the aromatic carbon atom which carries the carboxylic, sulphonic or phosphinic group is a carbon atom
- 30 which forms part of a single ring or a system of condensed rings of an aromatic nature, which in this specification must be taken to include plane rings or ring systems containing a system of delocalized  $\pi$ -electrons. As a rule
- 35 the rings or ring systems will be aryl groups, but heterocyclic structures of an aromatic nature, such as a pyridine ring are also possible.
- The aromatic rings or ring systems may in
- 40 addition to or instead of hydrogen atoms carry as substituents one or more other atoms, such as halogen atoms, or other groups, for example aryl, alkyl, alkoxy, cycloalkyl, hydroxy, amino, nitro, acyl, carboxyl and esterified carboxyl
- 45 groups.
- Of the carboxylic salts in particular the salts of acids containing a carboxyl group attached to a benzene ring have an attractive nucleating action. More specifically, the salts of benzene-
- 50 carboxylic acids which carry as a substituent a tertiary alkyl group or a carboxylic group which may or may not be esterified have proved excellent nucleating agents. Examples of such active salts are salts of p-tert-alkyl-
- 55 benzoic acid e.g. p-tert-butylbenzoic acid, phthalic acid, tetrachlorophthalic acid, and other substituted phthalic acids, and salts of the monoalkyl esters of phthalic acid and tetrachlorophthalic acid and other substituted
- 60 phthalic acids.
- Examples of salts of other benzenecarboxylic acids which, although preferred to a less extent, may nevertheless be employed, are salts of benzoic acid, p-nitrobenzoic acid, 2,4,6-trimethylbenzoic acid, 2,4-diethyl-6-isopropyl-
- benzoic acid, 2-octyl-4-hydroxybenzoic acid, 2-hydroxy-4-butylbenzoic acid, p-cyclohexylbenzoic acid, 2-aminobenzene-1,4-dicarboxylic acid, tetrachlorobenzene-1,4-dicarboxylic acid,
- 70 the two dichlorodiaminobenzene-1,4-dicarboxylic acid which are possible, pyromellitic acid and trimellitic acid.
- Further eligible nucleating agents are not only salts of benzenecarboxylic acids, but also salts of other aromatic carboxylic acids, such
- 75 as naphthalene-, anthracene- or phenanthrene-carboxylic acids. Examples thereof are naphthalene-1-carboxylic acid, naphthalene-2-carboxylic acid, 4-nitronaphthalene-1-carboxylic acid, 5,6,7,8 - tetrachloronaphthalene - 1,4-
- 80 dicarboxylic acid, 4-tert-butyl-naphthalene-1,6-dicarboxylic acid, anthracene-1-carboxylic acid, anthracene-9,10-dicarboxylic acid and 2-amino - 4 - isopropylphenanthrene - 1 - carboxylic acid.
- 85 Among the sulphonic salts in particular the salts derived from naphthalenesulphonic acids may be mentioned as effective nucleating agents. Examples of such very suitable salts are the salts of naphthalene-1-sulphonic acid,
- 90 naphthalene-2-sulphonic acid, 2-hydroxynaphthalene-6,8-disulphonic acid, 2-aminonaphthalene-4,8-disulphonic acid, naphthalene-1,3,5-trisulphonic acid, 6-cyclohexylnaphthalene-1-sulphonic acid, 4-tert-butyl-naphthalene-2-sulphonic acid, 2-phenylnaphthalene-
- 95 2-sulphonic acid, 4-nitro-naphthalene-2-sulphonic acid, 4-isopropyl-6-hydroxy-8-chloronaphthalene-1,3-disulphonic acid and 6-amino-8-octyl-naphthalene-1,3,5-trisulphonic acid.
- 100 Salts which are preferred to a less extent but which may also be used are those of benzenesulphonic acids, such as 2-methylbenzenesulphonic acid, 4-tert-butylbenzene
- 105 sulphonic acid, 4-amino-6-octylbenzene-1,3-disulphonic acid and 3-nitrobenzenesulphonic acid and furthermore also anthracene- and phenanthrene-, mono-, or di- or polysulphonic acids.
- Suitable phosphinic salts are substantially
- 110 the salts of benzenephosphinic acids, such as the benzenephosphinic acid itself and the compounds derived therefrom, in which the benzene ring carries an alkyl group as a substituent in the 2-, 4- or 5-position, such as 2-
- 115 methylbenzenephosphinic acid, 2,4-diethylbenzenephosphinic acid, 2,4-dimethyl-5-octylbenzenephosphinic acid and 2-methyl-4-hexyl-5-cyclohexylbenzenephosphinic acids.
- The mono-, bi- or trivalent metals in the
- 120 aforementioned salts of organic acids are in the first place alkali metals and alkaline earth metals, among which special preference is given to potassium, sodium and barium. However, the invention is non-restrictive in this
- 125 respect; also other alkali metals or alkaline earth metals such as lithium, cesium and calcium and furthermore also mono- to trivalent metals which do not belong to the alkali metals or alkaline earth metals, such as copper, iron,
- 130

magnesium, chromium, zinc, tin, nickel, cobalt and manganese, may be used as metallic components of the nucleating organic salts of said category (b).

5 It is further noted that the above discussion of the metal salts of organic acids exclusively refers to the neutral salts, while furthermore among these neutral salts the sodium salts are the most suitable for application in  
10 actual practice.

As a rule the nucleating compounds of the categories (a) and (b) defined hereinbefore are applied in a finely divided form, while it may be taken as a general rule that according as  
15 particles are smaller the nucleating action of the substances employed is greater. In this connection the use of nucleating agents with an average particle size below  $1\mu$  is particularly recommended.

20 The quantities in which the nucleating agents are present in the compositions according to the invention usually range from 0.0001 to 5 per cent by weight, calculated on weight of composition. Quantities of from 0.01 to 2  
25 per cent by weight are preferred.

The invention furthermore relates to a process for the preparation of the compositions discussed hereinbefore, which process comprises the incorporation of one or more of the compounds of the said categories (a) and (b)  
30 into the linear polyesters concerned. For this purpose any mixing technique known per se is in principle suitable, for example dry mixing, Banbury-mixing or mixing the polyesters with aqueous solutions or suspensions of the  
35 nucleating agents, followed by precipitation of the salts with a salting-out agent, such as acetone. These methods are not restricted to addition of ready salts to ready polyesters or to mixing of these compounds. It is also possible to cause the salts to be formed in situ in the presence of polyesters by reaction of acidic and basic components. Conversely, it is also  
40 possible to mix the salts with monomeric lactones and to perform the polymerization of the lactones, only then, in which case the polyesters are therefore formed in situ.

The practicability of the use of the present nucleating compounds is that various physical  
50 and mechanical properties of the crystalline polyesters are improved, which improvement occurs as soon as the polyesters in the novel compositions are caused to crystallize from the molten phase. Thanks to the presence of  
55 the nucleating compounds this crystallization leads to the formation of improved crystalline structures of spherulites with extremely small dimensions and hence also to the formation of polyesters of which the physical and mechanical properties that are related to the crystalline  
60 structure are improved.

Consequently, the invention also relates to a process for the preparation of compositions comprising one or more crystalline linear poly-  
65 esters which have been obtained by polymeri-

zation of lactones and which as compared with the said polyesters per se have improved physical and mechanical properties, which process comprises the preparation of a melt consisting  
70 of the novel compositions defined hereinbefore and the subsequent crystallization of the polyesters by cooling down of the melt.

Of the said improved mechanical properties may be mentioned, for example, an increased  
75 tensile and flexural strength, an increase in elongation at break, improved hardness, shear-stress coefficient, impact resistance, modulus of elasticity and yield stress. Improved physical properties are, for instance, improved surface structure and surface gloss of shaped objects. Furthermore, upon cooling down from  
80 the melt the compositions according to the invention solidify more rapidly than polyesters which do not contain nucleating compounds, as a result of which processing, by, for instance, compression-moulding or injection-  
85 moulding techniques may proceed faster. Besides, the novel compositions also have better shrinkage properties, which become evident in that upon cooling down of the novel compositions in moulds or dies solid polymer  
90 masses are formed in which no or hardly any voids occur, whereas shrinking of the crystalline polyesters per se shows a pronounced tendency to the formation of voids.

Shaping of the compositions according to the invention may take place before and/or during cooling down of the compositions, when  
100 crystallization of the polyesters occurs. If desired, this cooling procedure may take place very rapidly, that is, as rapidly as permitted by heat conduction. However, slow cooling is also possible. The duration of this slow cooling procedure may be from some minutes to  
105 some hours. Shaping may proceed in any manner known for this purpose and in any apparatus suited to this end. Articles of use may be manufactured by compression-moulding or injection-moulding, films may be obtained by blowing or by slit-extrusion, while the latter  
110 technique may also be employed to obtain fibres, threads, bars, strips, and the like, which, if desired, may be divided into granules, rods, flakes, chips, and the like. Since there are several other eligible shaping techniques, this enumeration should not be considered restrictive. Fibres and threads may be stretched to  
115 further improve their properties.

During shaping the compositions according to the invention may contain in addition to  
120 the nucleating compounds at the same time one or more other conventional additives, such as anti-oxidants, heat and light stabilizers, antistatic additives, dyes, pigments, carbon black or other fillers.  
125

#### EXAMPLE I.

In a number of experiments the nucleating action was determined of the compounds listed in the table. In each experiment 2 mg of these

compounds were mixed with 200 mg of polyester in a high speed vibrating ball mill.

5 The polyester, which had been prepared by polymerization of  $\alpha,\alpha$ -dimethyl- $\beta$ -propiolactone according to the method described in the British patent specification 1,028,928, had an intrinsic viscosity, measured in trifluoroacetic acid at 25°C, of 3.8 dl/g and a degree of crystallinity of 75% determined by X-ray diffraction  
10 of a sample of a polyester obtained by crystallization from the melt applying a cooling rate of 20°C/min. The polyesters contained 0.05 per cent by weight of tetramethyl thiuram disulphide and 0.2 per cent by weight  
15 of tri-(nonylphenyl)phosphite as heat-stabilizing additives.

5 mg of each composition were pressed into a platelet of 0.05 mm thickness between a cover glass and a slide at a temperature of  
20 260°C. Subsequently, the polyester was caused to crystallize by cooling the microscopic preparation thus obtained to the air at a cooling

rate of 100°C/min. Next, the average diameter of the spherulites was determined by visual microscopic observation.

In the experiment on the composition which did not contain nucleating compounds the microscopic preparation proved to consist merely of spherulites with strongly varying dimensions, the smallest spherulites having a diameter of 150 $\mu$  and the largest a diameter of 500 $\mu$ .

In the table the nucleating action of the compounds tested all of which had particle sizes of less than 1 micron, is represented by means of a relative scale. To the spherulites with an average diameter of between 50 and 150 $\mu$  a rating of 1 was assigned. A rating of 2 was assigned to spherulites with a size between 20 and 50 $\mu$ , a rating of 3 refers to spherulites with a diameter of between 5 and 20 $\mu$  and a rating of 4 was assigned to spherulites with a diameter below 5 $\mu$ .

TABLE 1

| Additive           | Action |
|--------------------|--------|
| Boron nitride      | 4      |
| Lithium chloride   | 3      |
| Sodium chloride    | 3      |
| Potassium chloride | 2      |
| Lithium bromide    | 3      |
| Sodium bromide     | 2      |
| Potassium bromide  | 3      |
| Lithium iodide     | 3      |
| Sodium iodide      | 3      |
| Potassium iodide   | 3      |

45

## EXAMPLE II.

In the manner described in Example I the nucleating action was investigated of the metal salts of carboxylic acids listed in Table

II all of which had a particle size of less than 1 micron. In these experiments, too, the quantities of the additives employed amounted to 2 mg per 200 mg polyester.

50

TABLE II

| Salts derived from:<br>Metal |   | Carboxylic Acids | Action |
|------------------------------|---|------------------|--------|
| K                            | Benzoic acid  |                  | 2      |
| Ba                           | ditto   |                  | 3      |
| Cu <sup>1</sup>              | ditto   |                  | 3      |
| Zn                           | 2,4,6-trimethylbenzoic acid                           |                  | 2      |
| Zn                           | p-nitrobenzoic acid                                   |                  | 1      |
| Na                           | 2,5-dihydroxybenzoic acid                             |                  | 3      |
| Zn                           | 2-hydroxy-3-methylbenzoic acid                        |                  | 2      |
| Zn                           | 2-hydroxy-4-methylbenzoic acid                        |                  | 2      |
| Zn                           | 2-hydroxy-4-tert-butylbenzoic acid                    |                  | 1      |
| Na                           | 4-tert-butylbenzoic acid                              |                  | 2      |
| Mg                           | ditto   |                  | 3      |
| Ba                           | ditto   |                  | 1      |
| Al <sup>3</sup>              | ditto   |                  | 2      |
| Cu <sup>1</sup>              | ditto   |                  | 3      |
| Cr <sup>3</sup>              | ditto   |                  | 2      |
| Sn <sup>2</sup>              | ditto   |                  | 2      |
| Cu <sup>1</sup>              | phthalic acid   |                  | 3      |
| Na                           | tetrachlorophthalic acid                              |                  | 3      |
| Ba                           | ditto   |                  | 1      |
| Cu                           | ditto   |                  | 2      |
| Na                           | monomethyl ester of phthalic acid                     |                  | 3      |
| Na                           | monoethyl ester of phthalic acid                      |                  | 3      |
| Na                           | monoethyl ester of tetrachlorophthalic acid           |                  | 2      |
| Na                           | mono-2-methoxyethyl ester of tetrachlorophthalic acid |                  | 3      |
| Na                           | pyromellitic acid                                     |                  | 3      |
| Ba                           | ditto   |                  | 1      |
| Cu <sup>1</sup>              | pyridine-3-carboxylic acid                            |                  | 3      |
| Na                           | pyridine-4-carboxylic acid                            |                  | 1      |
| Cu <sup>1</sup>              | ditto   |                  | 2      |
| Cu <sup>1</sup>              | pyridine-2,3-dicarboxylic acid                        |                  | 1      |

<sup>1</sup> = monovalent metal<sup>2</sup> = bivalent metal<sup>3</sup> = trivalent metal

## EXAMPLE III.

In a manner similar to the one described hereinbefore and using the same concentrations the nucleating action was determined of a number of aromatic sulphonic and phosphinic acids all of which had a particle size of less than 1 micron. 5

TABLE III

| Salts derived from:  |   |        |
|----------------------|---|--------|
| Metal                | Organic Acid                              | Action |
| (a) Sulphonic acids  |   |        |
| Na                   | 4-methylbenzenesulphonic acid             | 1      |
| Mg                   | 4-chlorobenzenesulphonic acid             | 1      |
| Na                   | 3-nitrobenzenesulphonic acid              | 1      |
| Ba                   | 4-diethylaminobenzenesulphonic acid       | 2      |
| Ba                   | 2-methoxy-5-methylbenzenesulphonic acid   | 3      |
| Mg                   | ditto                                     | 3      |
| Na                   | 1,2-dihydroxybenzene-3,5-disulphonic acid | 1      |
| Na                   | naphthalene-1-sulphonic acid              | 4      |
| Ba                   | ditto                                     | 4      |
| Mg                   | naphthalene-2-sulphonic acid              | 3      |
| Fe <sup>2</sup>      | ditto                                     | 3      |
| Co <sup>2</sup>      | ditto                                     | 3      |
| Cu <sup>1</sup>      | ditto                                     | 2      |
| Na                   | anthraquinone-1-sulphonic acid            | 3      |
| K                    | ditto                                     | 2      |
| K                    | 2-hydroxynaphthalene-6,8-disulphonic acid | 3      |
| Na                   | 2-aminonaphthalene-6,8-disulphonic acid   | 4      |
| Na                   | naphthalene-1,3,5-trisulphonic acid       | 4      |
| (b) Phosphinic acids |   |        |
| Na                   | benzenephosphinic acid                    | 3      |
| K                    | ditto                                     | 3      |
| Na                   | 2-methylbenzenephosphinic acid            | 2      |

<sup>1</sup> = monovalent metal

<sup>2</sup> = bivalent metal

## EXAMPLE IV.

The same polyester as described in Example I, which also contained the same heat-stabilizing system, was mixed homogeneously with 1%w of sodium naphthalene-1-sulphonate having a particle size of less than 1 micron.

The composition thus obtained was milled to sheets after which a number of milled sheets were piled up and shaped to a sheet of 1 mm thickness in a hydraulic press at 270°C. The sheet was subsequently cooled down to a temperature of 60°C in the press, during which a phase transition from the molten phase (the melting point of the polyester is 240°C) to the solid crystalline phase took place. Subsequently, the sheet was removed from the press and further air-cooled to room temperature.

The sheet so obtained had a bright glossy and perfectly smooth surface with a uniform colour.

For comparison the experiment was repeated without sodium naphthalene sulphonate but under otherwise similar conditions.

The sheet made in this comparative experiment had a dull and rough, granular surface, in which large bright white spots consisting of spherulites with a size of from 0.25 to 1 mm could be observed, which spots showed up against an inhomogeneously coloured background.

## WHAT WE CLAIM IS:—

1. A composition comprising at least one crystalline linear polyester obtained by the polymerization of a  $\beta$ -lactone, and at least one compound belonging to the following categories:—

- (a) alkali metal chlorides, bromides or iodides or boron nitride, and
- (b) salts of mono-, bi- or trivalent metals and aromatic carboxylic, sulphonic or phosphonic acids.

2. A composition as claimed in claim 1, in which the compound of category (a) is sodium or potassium chloride.

3. A composition as claimed in claim 1, in which the compound of category (a) is boron nitride.

4. A composition as claimed in claim 1, in which the compound of category (b) is a salt of a sulphonic acid.

5. A composition as claimed in claim 1, in which the compound of category (b) is a salt of a naphthalenesulphonic acid.

6. A composition as claimed in claim 1, in which the compound of category (b) is a salt of a carboxylic acid.

7. A composition as claimed in claim 6, in which the compound is a salt of a benzene-carboxylic acid.

8. A composition as claimed in claim 7, in

which the compound is a salt of a 4-tert-alkylbenzene-1-carboxylic acid.

9. A composition as claimed in claim 6, in which the compound is a salt of phthalic acid or a substituted phthalic acid.

10. A composition as claimed in claim 6, in which the compound is a salt of tetrachlorophthalic acid.

11. A composition as claimed in claim 6, in which the compound is a salt of a monoalkyl ester of phthalic acid.

12. A composition as claimed in claim 6, in which the compound is a salt of a monoalkyl ester of tetrachlorophthalic acid.

13. A composition as claimed in claim 1, in which the compound of category (b) is a salt of a benzenephosphinic acid.

14. A composition as claimed in any of claims 4 to 13, in which the compound of category (b) is a salt of an alkali metal or alkaline earth metal.

15. A composition as claimed in any of claims 4 to 14, in which the salt is a sodium salt.

16. A composition as claimed in any of claims 1 to 15, in which the salt is present in a quantity of from 0.0001 to 5 per cent by weight, calculated on total weight of composition.

17. A composition as claimed in claim 16, in which the quantity amounts to from 0.01 to 2 per cent by weight.

18. A composition as claimed in any of claims 1 to 17, in which the polyester has been obtained by polymerization of an  $\alpha,\gamma$ -dialkyl- $\beta$ -propiolactone, in which each of the alkyl groups contains at most 4 carbon atoms.

19. A composition as claimed in any of claims 1 to 18 substantially as described in any of the Examples.

20. A process for the preparation of a composition as claimed in any of claims 1 to 19, which comprises the incorporation of at least one compound of the relevant category (a) or (b) into the polyester.

21. A process for the preparation of a composition containing at least one crystalline linear polyester obtained by polymerization of lactones, which composition as compared with the said polyester per se has improved physical and mechanical properties, which process comprises the preparation of a melt consisting of a composition as claimed in any of claims 1 to 19 and the subsequent crystallization of the polyester by cooling the melt.

22. A composition whenever obtained as claimed in claim 21.

23. An object consisting entirely or partly of compositions as claimed in claims 1 to 19 or 22.

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